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SHORT COMMUNICATION

# SIGNIFICANCE OF THE QUALITY OF FLORISIL® IN ORGANOCHLORINE PESTICIDE ANALYSIS

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During the analysis of chlorinated pesticides in animal fat tissue applying the matrix solid-phase dispersion method, and notwithstanding the use of a gas chromatograph with a highly selective capillary column, two peaks occur: one with a retention time very similar to that of lindane, and the other almost identical to that of dieldrin. Repeated analyses of the same sample with a GC/MS system revealed that neither lindane nor dieldrin were present. It was proven that those peaks resulted from florisil of local origin used for analysis, but not from the original Florisil®. The removal of the first peak (»lindane«) was possible through heating of florisil of local origin at 680 °C for 4 hours, whereas some other method would be required for the removal of the other peak (»dieldrin«). The incident proved that, in such demanding analyses, it is extremely important to use original, high quality substances to avoid possible interference and misinterpretation of results.

*Key words:*
dieldrin, GC/MS identification, lindane, multiresidue extraction

Ever since World War II, various chlorinated compounds have been used as pesticides. In view of their persistence in natural environment (1), solubility in fats and tendency to accumulate in human (2–6) and animal fat tissue (7–8), as well as of their harmful effects on the ecosystem in general, their extensive use in agriculture has been restricted or banned in many countries since the early seventies. However, since they continue to be used (9) in our country, among others, regular control of their levels in animal fat tissue, milk, and milk products intended both for the domestic market and for the EU and US market is mandatory. DDT and its metabolites, lindane and other HCH isomers, aldrin, dieldrin, endrin, and toxaphene are routinely

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included in determination of residues in animal fat tissue within the frame of Croatian Monitoring Programme for Residues in Meat and Foodstuffs of animal origin (10). Regardless of certain similarities regarding their solubility in fats (and in organic solvents), their versatility, the occurrence of other chlorinated compounds, and the complexity of the matrix used for their analysis make their determination very demanding. The main limiting factor in the determination of pesticide residues is their extraction from complex biological systems such as fat. Most methods require a large quantity of samples and solvents, involve many steps, and are time-consuming (11–14). Recently, a multiresidue extraction technique called matrix solid-phase dispersion (MSPD) was developed (15–17). The purpose of this work was to evaluate the quality of domestic florisil for the clean-up procedure and – through the application of a GC/MS method – to eliminate the doubt about possible presence of lindane and dieldrin.

## MATERIAL AND METHODS

To prepare samples for the analysis of pesticides in fat tissue, we adopted the so called matrix solid-phase dispersion method (MSPD) (18). The procedure involves grinding of fat tissue with silica solid supports (40 $\mu$m particle size) to which lipid solubilising polymer octadecylsilyl is chemically bound. The $C_{18}$/fat matrix blend was fashioned into a column by adding the blend to a 10 ml syringe barrel containing 2 g of activated florisil of domestic origin, or original Florisil®. A gas chromatograph ATI Unicam 610 with electron-capture detector (ECD) and a capillary column DB-608 (30 m x 0.32 mm I.D.; film thickness: 0.5 $\mu$m) was used to determine pesticides. Gas chromatograph ATI Unicam 615 with the same capillary column and a mass spectrometer Automass System 2 with quadrupole mass analyser were used for GC/MS analysis.

Working conditions for the gas chromatograph were as follows:

t(detector)=330 °C;
t(injector)=250 °C;
$t_{INITIAL}$ (column)=120 °C (1 min) with Dt=5 °C/min;
$t_{FINAL}$ (column)=270 °C (12 min);
splitless time – $T_{DISCONN.}$=1 min;
carrier gas: He (70000 Pa);

Working conditions for GC/MS system included:

t(injector)=250 °C;
$t_{INITIAL}$ (column)=120 °C (1 min) with Dt=5 °C/min;
$t_{FINAL}$ (column)=270 °C (12 min);
splitless time – $T_{DISCONN.}$=1 min; carrier gas: He (50000 Pa);
ionization energy=70 eV;
filament=800 $\mu$A, photomultiplier=750 V;
vacuum=1.1066 Pa;
t(source)=130 °C;
t(interface)=250 °C.

## RESULTS AND DISCUSSION

Figures 1 and 2 show the ECD chromatograms obtained after a blank sample treated with activated florisil of domestic origin (Fig. 1) and a blank sample treated with activated original Florisil® (Fig. 2) were injected into the gas chromatograph. Figure

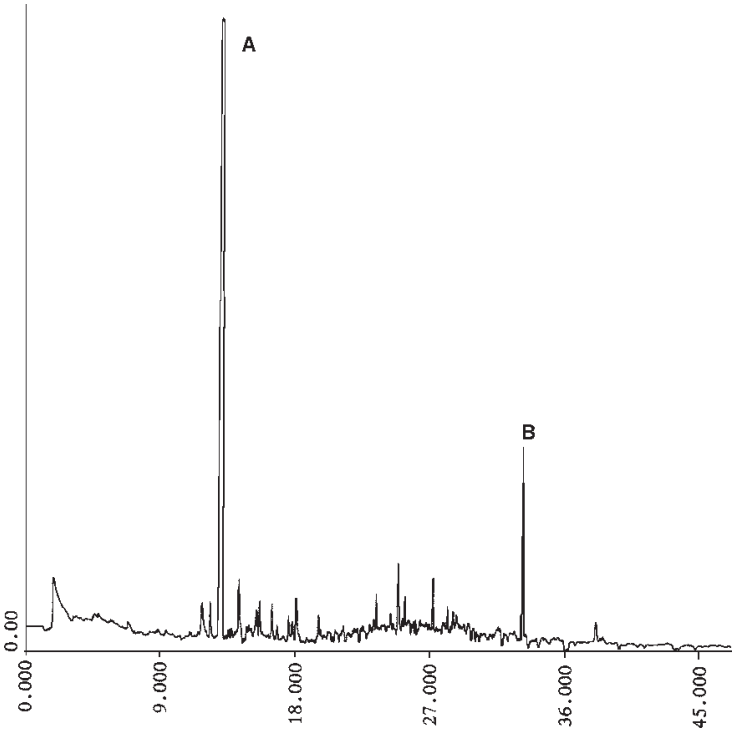


Figure 1 *ECD-chromatogram of blank sample treated with nonheated domestic florisil*

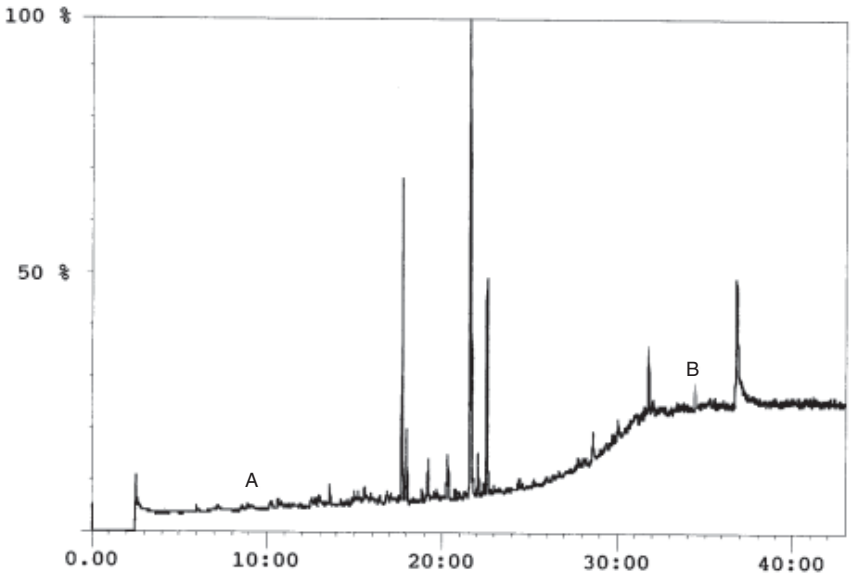


Figure 2 *ECD-chromatogram of blank sample treated with nonheated original Florisil®*

3 shows the ECD chromatogram obtained after preparation of a blank sample with domestic florisil heated for 4 hours at 680°C. Figures 4 and 5 show the mass spectra of both peaks: A (»lindane«) and B (»dieldrin«).

After matrix solid-phase dispersion, chromatograms of the sample prepared with florisil of domestic origin clearly show two peaks. Peak A, according to standards, has retention time very similar to that of lindane, whereas peak B, again in terms of retention time, is almost identical to dieldrin (Fig. 1). We noted that domestic florisil might cause higher or lower, not always proportional, peaks in places which are, by their retention time, similar to lindane (peak A: $t_r = 12.9$ min) and almost identical to

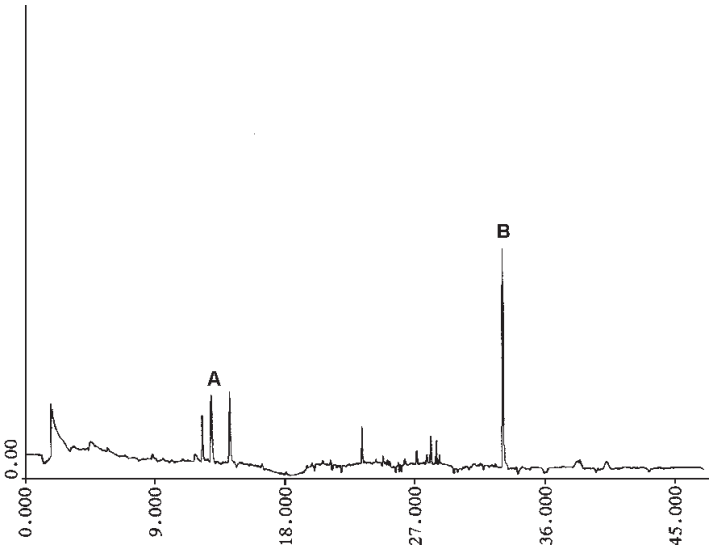


Figure 3 *ECD-chromatogram of blank sample treated with heated florisil of domestic origin*

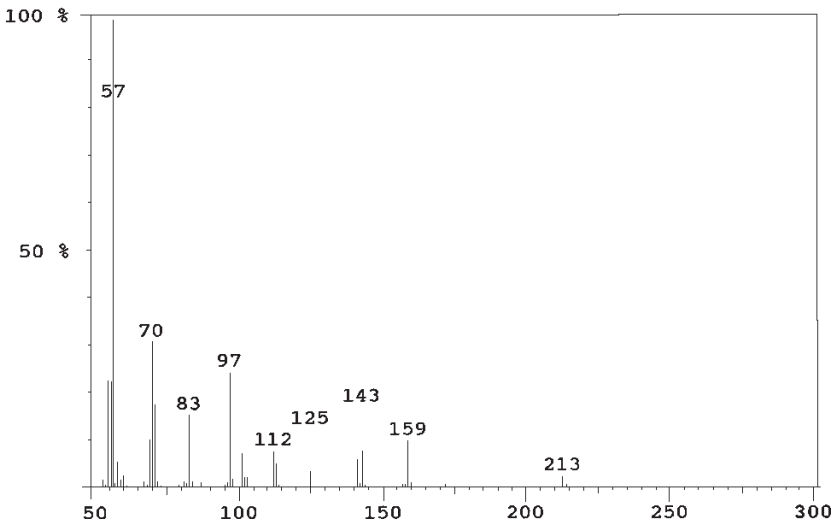


Figure 4 *EI-mass spectrum of peak A (»lindane«)*

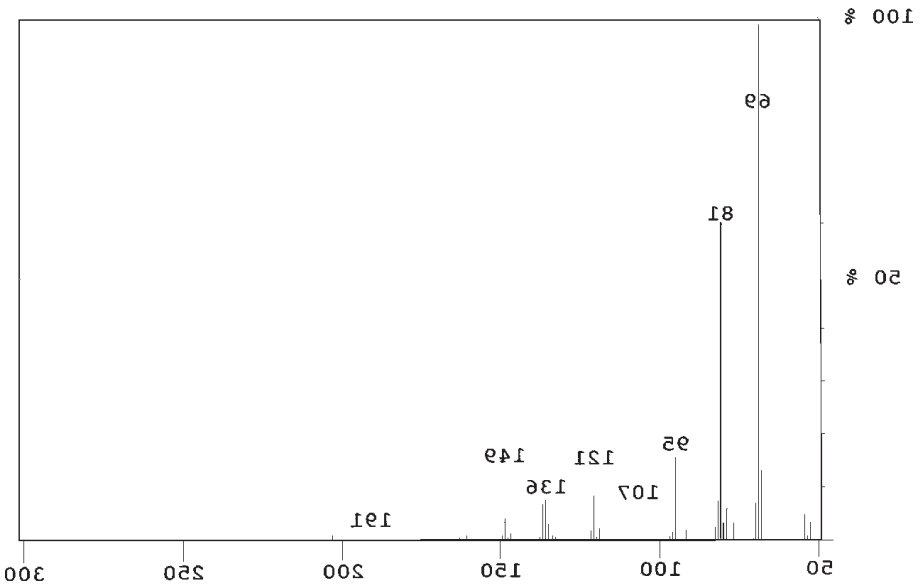


Figure 5 EI-mass spectrum of peak B (»dieldrin«)

dieldrin (peak B: $t_r$=34.3 min). The next step involved heating of domestic florisil for 4 hours at 680 °C, which resulted in almost complete removal of the peak A which, in a less selective column, could be easily confused with lindane. Unfortunately, this was not the case with the peak B, which coincided with dieldrin, even on a 30-metre capillary column DB-608 (Fig. 3). Considering that this dilemma was not resolved with GC-ECD method, we proceeded with the application of a GC/MS system in selected ion-monitoring mode. After having inserted the values of m/z fragments typical for lindane (m/z=111, 181, 219, and 254) and for dieldrin (m/z=79, 108, 263, and 345), we received negative response in both cases. Not a single fragment was found to precisely correspond to the given m/z with either peak A or peak B. It was therefore easy to conclude that the actual peaks were neither lindane nor dieldrin. Although we modified working conditions, reducing the energy of the electrons and applying chemical ionization with methane, we were not able to exactly identify either peak. The fact remains, however, that peaks A and B were neither lindane nor dieldrin and that the present »pesticides« raised from the florisil of domestic origin, not from the original Florisil®. This was yet another proof that, in such demanding analyses, it is extremely important to use solvents and reagents of high purity, that is, pesticide grade, to avoid possible interference and misinterpretation of results.

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*Sažetak*

## ZNAČENJE KVALITETE FLORISILA® TIJEKOM ODREĐIVANJA KLORIRANIH PESTICIDA

Tijekom određivanja kloriranih pesticida u životinjskom masnom tkivu metodom *matrix solid-phase disperson* (MSPD) usprkos uporabi plinskog kromatografa s visoko selektivnom kapilarnom kolonom pojavljuju se dva pika (šiljka): jedan retencijskog vremena vrlo sličnog lindanu, i drugi gotovo identičan s dieldrinom. Dobiveni rezultati pokazuju da se ovi pikovi (šiljci) pojavljuju upotrebom domaćeg, ali ne i originalnog florisila (Florisil®). Primjenom GC/MS sistema dokazano je da se ne radi ni o lindanu ni o dieldrinu. Uklanjanje prvog pika (»lindan«) moguće je žarenjem florisila tijekom 4 sata na 680 °C, dok je očito da je za uklanjanje drugog pika (»dieldrin«) potreban neki drugi postupak. Ovo je još jedan dokaz koliko je neobično važno u tako zahtjevnim analizama rabiti vrlo čiste kemikalije i standarde da bi se izbjegle moguće interferencije i pogrešne interpretacije rezultata.

*Ključne riječi:*
dieldrin, GC/MS identifikacija, lindan, životinjsko masno tkivo

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